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TECHNICAL REPORT 23

Contract N9onr-85801  
Project Designation NR031-364

THE MAINTENANCE OF A LOW OXYGEN  
ATMOSPHERE USING SALCOLINE

by

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Mine Safety Appliances Company  
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TABLE OF CONTENTS

ABSTRACT	Page
INTRODUCTION	1
A. Authorization	1
B. Statement of the Problem	1
C. Known Facts Bearing on the Problem	1
D. Literature Research on Salcomine	2
E. Program	3
METHODS	4
A. Apparatus	4
B. Procedure and Operation	4
DISCUSSION OF DATA	5
DESIGN UNIT	5
FUTURE RESEARCH	6
APPENDIX	

7  
7  
ATION

# ABSTRACT

This report is a study of the performance of Salcomine in controlling the oxygen content in a 4000 cu.ft. chamber. Salcomine is a regenerative chelate possessing the ability to absorb oxygen reversibly.

With an initial 7% oxygen atmosphere, data is reported on runs with approximate flow rates of 3, 2 and 1 cfm through the absorbing unit under pressures of 100, 75, 50 and 40 psig. From the above runs the optimum operating conditions appeared to be 100 psi, with a circulating rate of 2 cfm. A few comparative runs were made with a 5 and 10% oxygen atmosphere at these optimum conditions.

Based on the optimum operating conditions and on absorption capacity of 1.3% oxygen by weight, a unit was designed in conjunction with Mark A for maintaining a 5% oxygen atmosphere, over a period of 60 - 90 days, with a continuous air leak of 0.1 cfm into the specified chamber.

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## INTRODUCTION

### A. Authorization

This project was authorized by the task order of Contract N9anr-85801.

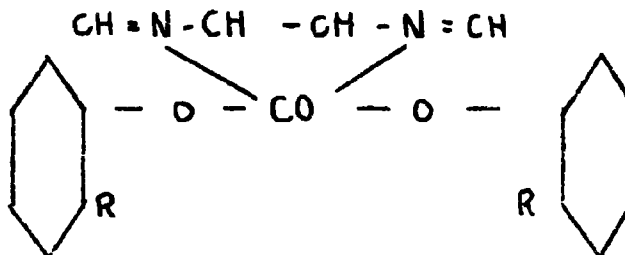
### B. Statement of the Problem

A program was proposed to determine the optimum operating conditions when using Salcomine to control the oxygen content in a 4000 cu.ft. chamber. The data was to be used to design a unit to meet Mark A conditions.

### C. Known Facts Bearing on the Problem

It has been found(1) that the hazards arising from sodium fires can be minimized if the atmosphere over the sodium is less than 7% oxygen. To maintain a low oxygen atmosphere, it was decided to use a regenerative system in which oxygen is absorbed by a granular solid chemical, and then regenerated in a cyclical process.

The absorbents, which are metallic chelates, possess the ability to absorb oxygen reversibly(2). They are structurally similar and can be represented by the formula



where R is hydrogen in the case of Salcomine, a methoxy group ( $\text{CH}_3\text{-O-}$ ) in the case of methomine, and an ethoxy group ( $\text{CH}_3\text{-CH}_2\text{-O-}$ ) in the case of ethomine. These absorbents are crystalline solids which can readily be caked or granulated.

The chemicals absorb oxygen to the extent of three to four weight per cent from air at atmospheric or higher pressures and room temperature. On heating to temperatures varying from 130° to 200°F., the compounds release, or desorb, the oxygen. The desorption is usually carried out under vacuum to minimize the destructive oxidation of the chemical.



The additional amount of oxygen that can be absorbed per unit of chemical per cycle decreases as saturation is approached. In use the absorption period is usually terminated at 70 per cent of saturation.

A detailed discussion follows on Salcomine which was the absorbent selected for maintaining a low oxygen content in the chamber.

#### D. Literature Research on Salcomine

Salcomine is a maroon-colored microcrystalline material which is somewhat soluble in pyridine, chloroform and benzene as reported by Diehl and Co-workers<sup>(3)</sup>. The material, in a dry state, absorbs oxygen, turning from maroon to black in color. The deoxygenated form of the material is paramagnetic, the oxygenated form diamagnetic. The compound is quite toxic; inhalation of the finely divided dust should be avoided.

Salcomine will absorb oxygen reversibly and nitric oxide and nitrogen dioxide irreversibly. Carbon monoxide, nitrous oxide and sulfur dioxide are not absorbed<sup>(3)</sup>. Pure carbon dioxide at atmospheric pressure and room temperature does not appreciably affect the absorbing capacity of Salcomine<sup>(4)</sup>.

The absorption of oxygen is a reversible process with a heat of reaction of 18.5 kilocalories/gm.mol of oxygen absorbed.

It has been shown by Diehl and Co-workers, that Salcomine is a binuclear compound in which a molecule of water acts as a bridging group ( $\gamma$ -Aquo) between two cobalt atoms, each of which is surrounded by the quadridentate, chelating molecule of the Schiff base. This material has the unique property of reversibly absorbing and releasing oxygen. The addition of the oxygen is thought to take place by the formation of a peroxo group, which makes a second bridge between the two cobalt atoms and fills the sixth coordination position of each cobalt atom. Thus, one oxygen molecule is absorbed for each two cobalt atoms, corresponding to a gain in weight of 4.79 per cent<sup>(3)</sup>.

General rules are that the oxygen be absorbed at relatively low temperatures (50-75°F) and increased pressures. Regeneration should be carried out at approximately 200°F under 0.1 atmospheric pressure<sup>(5)</sup>. The Salcomine should be maintained at the regeneration temperatures as short a time as possible, and should be cooled before the absorbing cycle is started.

Adverse effects on the efficiency and life of Salcomine are produced by oily or dirty air, water vapor, ammonia, and ultra violet radiation(6). The materials which are absorbed irreversibly also decrease the efficiency of the chemical. Excessively oily or dirty air will affect the life of the cholate in continuous operation although there is no harmful effect for short exposure times. Water vapor will be absorbed by Salcomine but is removed in the desorption cycle. If the dew point of the atmosphere is higher than the desorption temperature the condensation of water has a deleterious effect on the chemical(7). Water vapor in the desorption atmosphere has only a slight catalytic effect on the rate of chemical deterioration, but the amount of active Salcomine for oxygen absorption can be lowered by as much as 75%.

Although a number of factors contribute to deterioration of the chelates, the most important seems to be an irreversible oxidation by molecular oxygen. Micro-photographic studies showed the fracture of crystals into smaller fragments during oxygenation. The Salcomine will fall to approximately 75% efficiency after 1500 cycles of regeneration(2).

#### E. Program

A program was proposed to determine the engineering design factors for a unit to operate under the following conditions submitted by KAPL and EB.

1. The gas from the cooler (feed to oxygen absorbers) at 70°F.
2. Fresh water at 180°F available up to 3 GPM for the desorption cycle.
3. Chilled water at 50°F available up to 3 GPM for the absorption cycle.

With an initial 7% oxygen content in the chamber, the range of variables was outlined to determine the optimum operating conditions.

Inlet Pressure psi	Circulating Rate CFM (free air)
100	2,1
75	2.5, 2,1
50	3, 2,1
30	3, 2,1

After determining the optimum conditions, a few tests were proposed with a 5 and 10% oxygen atmosphere in the chamber. The range of the MSA oxygen indicator (0-10% oxygen) was used to set the limit of the oxygen content in the feed gas.

## METHODS

### A. Apparatus

Three standard shell and tube heat exchangers (Figures 1 and 3) were packed with Salcomine in the tubes to depths of 22, 15 and 10 inches, containing 9.2, 6.4 and 4.2 pounds of Salcomine respectively. The Salcomine was made in our own laboratory. Water was circulated through the shell side for temperature control of the bed. A compressor circulated the atmosphere of the chamber through each of the three units (Figures 2 and 4). The MSA oxygen indicator (range 0 - 10%) was used for oxygen analyses, the instrument being checked with an Orsat analysis during initial runs.

### B. Procedure and Operation

After checking the entire system for leaks, the chamber was evacuated to approximately 10 inches of mercury (ABS) and filled with nitrogen to obtain an approximate 7% oxygen atmosphere. Thereafter, a slight pressure was kept in the chamber by introducing nitrogen when needed throughout the test program.

The test program was started after the initial activation of the chemical. The average absorption was carried out for 60 minutes with inlet air and cooling water temperatures of approximately 75°F and 50°F respectively. The inlet and outlet gas temperatures, pressure and flow were recorded with the water temperature and flow. The inlet oxygen was analyzed at the beginning and end of each run, while the exit gas stream was sampled continuously and recorded every 5 minutes.

All regenerations were carried out at approximately 160°F, under 3 inches mercury pressure (ABS) and the Salcomine was cooled to about 50°F before the absorbing cycle was started. The time necessary for regeneration was about 15 minutes, which was checked by installing a wet gas meter on the exhaust and measuring the flow of gas during desorption. The flow rate of the cooling and heating water was approximately 3 GPM.

## DISCUSSION OF DATA

Tables I, II and III show the summarized data of the three Salcomine absorbers. The maximum absorption was about 1.5%, as compared to the value of 4.03% obtained in the laboratory with 100% oxygen at 40 psi pressure. All runs were made to nearly complete oxygenation and runs 3a and 25 (Figure 5) were carried out until the exit and inlet oxygen content were almost equal. At the end of the runs the total absorption was approximately 1.4% at the higher pressure and 1.0% at the lower pressure.

There have been several suggested causes for the low capacity of the Salcomine as compared with the capacity obtained in the laboratory under ideal conditions. One suggestion was that during the short period of pressurizing the absorber enough oxygen was absorbed by the Salcomine to indicate a low capacity. This is not true, however, since less than 1% of the total volume of gas passing through the Salcomine has gone through during the pressure build-up. A second suggested cause, and the one thought to be most valid, is that due to the method used for packing the Salcomine in the tubes, all the tubes may not be used. There is no reason to believe that the Salcomine is not completely regenerated, this could also be a cause. The only available pressure equilibrium data is at zero and 25°C and is shown in Figure 6.

A typical absorption curve of each unit is illustrated in Figure 7, taken from the second run on each unit. From the data, it appears that the pressure has a decided effect on the rate of absorption and total oxygenation.

It also appears that the bed depth is not a controlling factor in this experiment. The optimum operating conditions, from Table I, appear to be as follows.

Gas pressure	100 psig
Circulating Rate	2 CFM
Cycle Time	1½ Hrs.(absorption and desorption)

At these operating conditions, a few runs were made with an initial 5 and 10% oxygen. As would be expected, the absorption rate varies with the initial oxygen content (Figures 8 and 9).

## DESIGN UNIT

Based on the optimum operating conditions and unit #1 with a 1.3% absorption capacity, a new Salcomine unit was

designed under conditions proposed by KAPL.

1. Maintain a 5% oxygen atmosphere with 0.1 CFM air leakage to the chamber.
2. 60-90 day life on the Salcomine.

The unit is rectangular in shape, 15-5/8 in. x 11 in. x 8-5/8 in., and is capable of holding approximately 10 lb. of Salcomine. Based on the experimental data the unit should readily handle the leak operating with 16 cycles/day with 1 hour absorption and 1/2 hour for desorption.

The Salcomine will be packed on the shellside with water flowing through the tubes for temperature control of the bed. This method of packing may yield a better efficiency of the Salcomine. Four unions will permit the unit to be replaced readily. (Figure 10).

#### FUTURE RESEARCH

MSA will undertake the proof testing of the new Salcomine unit along with a Baker unit supplied by KAPL. This latter unit is a catalytic unit which removes the oxygen as carbon dioxide by burning diesel fuel over a catalytic bed at approximately 840°F. The carbon dioxide is then removed with a water scrubber and the air, primarily nitrogen, is returned to the chamber.

The conditions of the test will approximate Mark A conditions as nearly as possible. The chamber will be used and fitted with a metered "leak". Data will include the time to reduce the oxygen from 7% to 5% and the effect of humidity. Any additional tests required can be determined later.

7  
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RESULTS

TABLE I

ABSORPTION

Unit #1

22 in. Bed - 9.2 lb. Salcomine

Run No.	% O <sub>2</sub> in	Free Air CFM	Press Psig	Air OF	Water		Time Min.	Oxygen Absorbed by Salcomine	
					OF	GPM		Wt. %	lb. O <sub>2</sub>
1	6.11	2.0	92	72	48	3.0	60	1.01	0.092
2	6.74	2.0	98	71	49	3.0	60	1.92	0.176
3	6.85	2.0	98	72	45	3.0	60	1.27	0.117
3a	6.85	2.0	98	72	45	3.0	100	1.38	0.130
4	6.70	1.0	97	74	50	3.0	60	0.96	0.089
5	6.60	1.1	98	73	49	3.0	60	1.41	0.129
6	6.50	2.0	69	75	52	3.0	60	1.31	0.121
7	6.34	2.65	73	73	49	3.0	60	1.32	0.12
8	6.68	2.0	72	74	50	3.0	60	1.58	0.145
9	6.30	1.0	71	76	51	3.0	60	1.23	0.113
10	6.57	1.0	75	74	50	3.0	60	1.32	0.122
11	6.50	2.55	58	71	50	3.0	40	1.04	0.096
12	6.20	2.0	50	73	49	3.0	60	1.23	0.113
13	6.40	1.0	50	71	50	3.0	60	1.15	1.105
14	6.50	2.75	39	71	53	3.0	60	0.73	0.074
15	6.17	2.8	25	71	49	3.0	60	0.69	0.063
16	6.75	2.0	29	73	50	3.0	60	0.87	0.080
17	6.35	1.1	31	73	49	3.0	60	0.88	0.081
18	4.89	2.0	97	73	50	3.0	60	1.09	0.10
19	5.00	2.0	70	74	50	3.0	60	0.91	0.084
20	4.90	2.0	49	74	50	3.0	60	0.55	0.051
21	9.35	2.0	97	72	51	3.0	60	1.50	0.138
22	9.15	2.0	95	73	49	3.0	60	1.50	0.138
23	0.60	2.0	70	72	52	3.0	60	1.28	0.118
24	9.3	2.0	70	72	52	3.0	60	1.43	0.132
25	8.85	2.4	27	73	54	3.0	110	.97	0.089

RESULTS

TABLE II

ABSORPTION

Unit #2

15 in. Bed - 6.4 lb. Salcomine

Run No.	% O <sub>2</sub> in	Free Air CFM	Press Psig	Air OF	Water		Time Min.	Oxygen Absorbed by Salcomine	
					OF	GPM		Wt. %	lb. O <sub>2</sub>
1	6.11	2.0	91	72	50	3.0	45	0.89	0.057
2	6.73	2.0	96	73	49	3.0	45	1.51	0.097
3	6.95	1.0	95	74	49	3.0	45	1.29	0.083
4	6.50	1.1	97	72	49	3.0	45	1.18	0.076
5	6.20	2.65	72	73	50	3.0	45	0.96	0.061
6	6.70	1.95	70	75	50	3.0	45	1.39	0.085
7	6.50	2.0	60	75	51	3.0	45	1.23	0.079
8	6.57	1.0	75	74	50	3.0	45	1.14	0.105
9	6.10	1.0	70	77	50	3.0	45	1.02	0.066
10	6.51	2.5	64	71	50	3.0	45	1.03	0.066
11	6.45	2.75	40	71	52	3.0	45	0.69	0.044
12	6.10	2.0	50	76	51	3.0	45	1.01	0.065
13	6.34	1.0	47	71	51	3.0	45	0.94	0.06
14	6.08	3.8	24	73	50	3.0	30	0.30	0.019
15	6.75	2.0	29	74	49	3.0	45	0.84	0.054
16	6.30	1.0	31	73	51	3.0	45	0.60	0.039
17	4.71	2.0	95	74	50	3.0	45	0.81	0.052



7

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# RESULTS

TABLE III

## ABSORPTION

Unit #3

10 in. Bed - 4.2 lb. Salcomine

Run No.	% O <sub>2</sub> in	Free Air CFM	Press Psig	Air OF	Water		Time Min.	Oxygen Absorbed by Salcomine	
					OF	GPM		Wt. %	lb.O <sub>2</sub>
1	6.5	2.05	94	72	50	3.0	45	1.12	0.050
2	6.75	2.0	97	73	49	3.0	40	1.53	0.064
3	6.77	1.0	99	78	50	3.0	45	1.28	0.054
4	6.40	1.0	98	74	49	3.0	35	1.13	0.048
5	6.35	2.0	71	74	51	3.0	45	1.51	0.067
6	6.68	1.95	71	77	50	3.0	40	1.20	0.051
7	6.21	1.0	73	78	50	3.0	45	1.21	0.051
8	6.43	0.95	74	77	52	3.0	45	1.26	0.053
9	6.39	2.75	40	71	52	3.0	30	0.522	0.022
10	6.60	2.55	57	70	50	3.0	35	0.864	0.036
11	6.10	2.0	49	75	52	3.0	45	0.98	0.041
12	6.0	1.0	49	73	50	3.0	45	1.10	0.046
13	6.05	2.8	23	72	50	3.0	30	0.18	0.008
14	6.75	2.0	29	73	50	3.0	45	0.77	0.033
15	6.13	2.6	26	70	50	3.0	45	0.75	0.032
16	6.25	1.0	32	74	49	3.0	45	0.75	0.031
17	4.73	2.0	97	74	50	3.0	45	0.869	0.037

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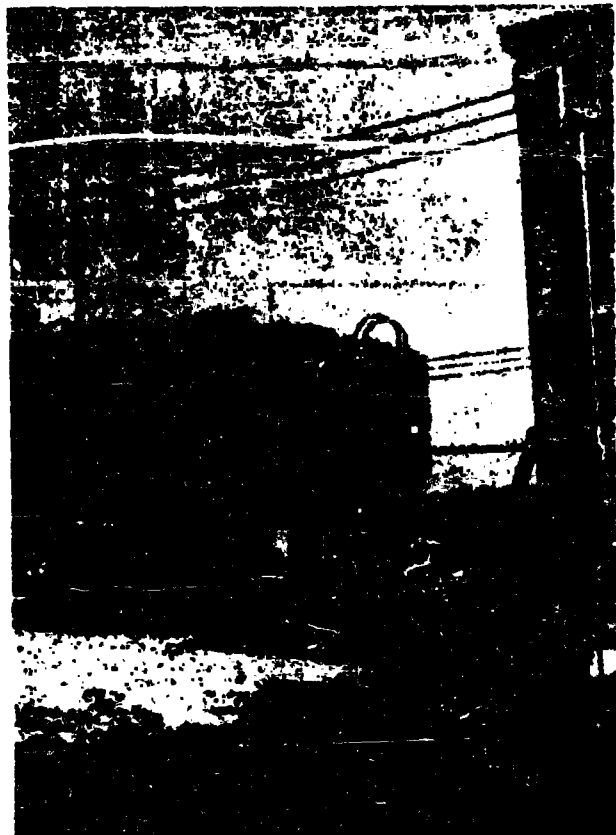
Salcomine Test System



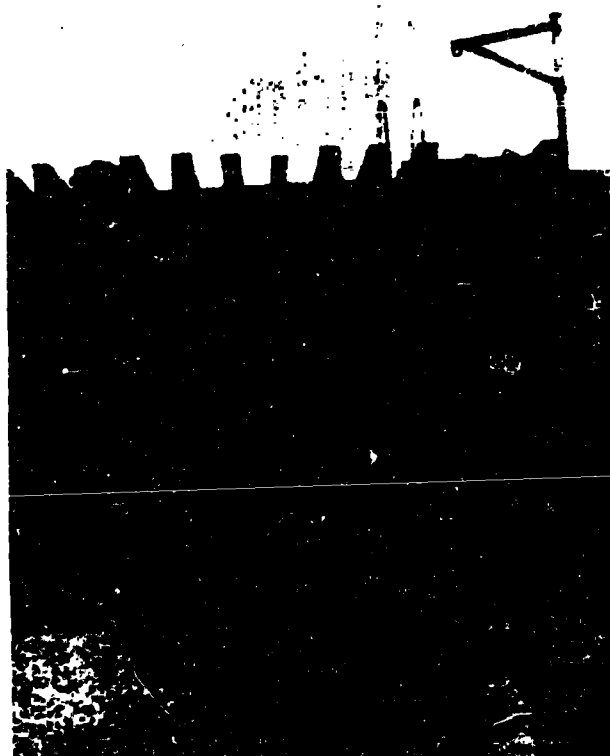
Salcomine Test Absorbers

Figure 1

Salcomine Test System



Southeast Side of  
the LRC Chamber



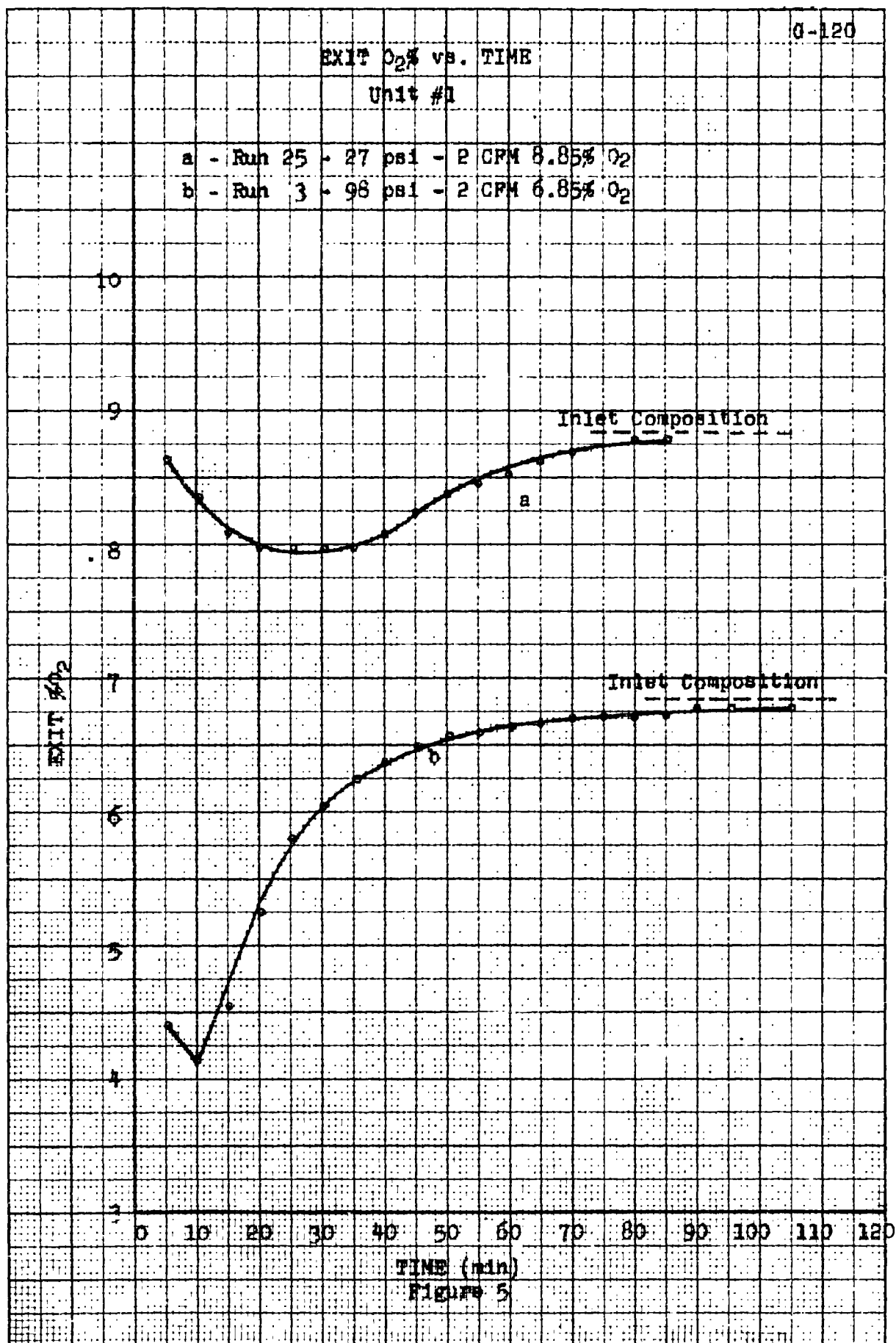
West Side of The  
LRC Chamber

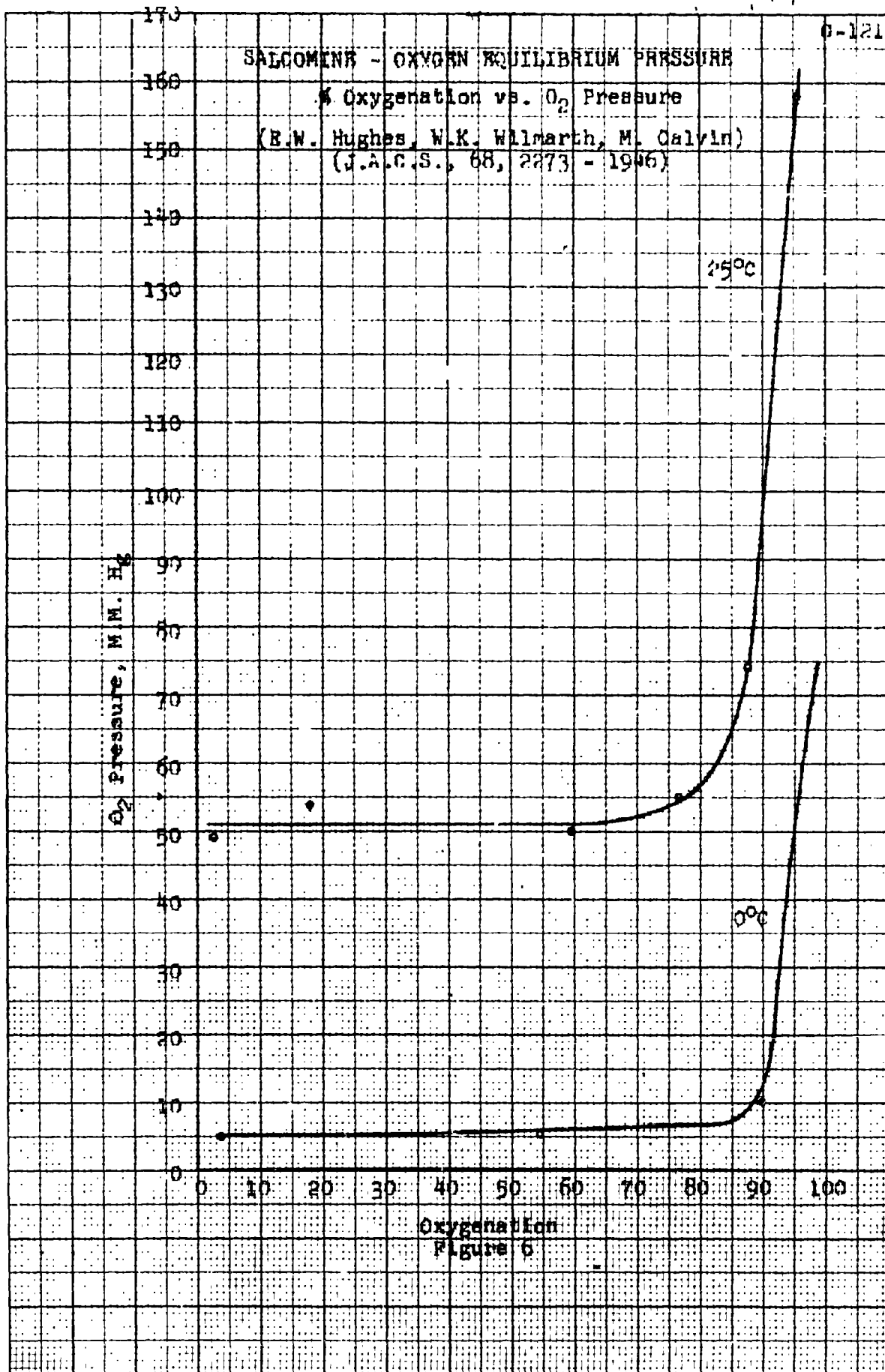
Figure 2.



FIGURE 4

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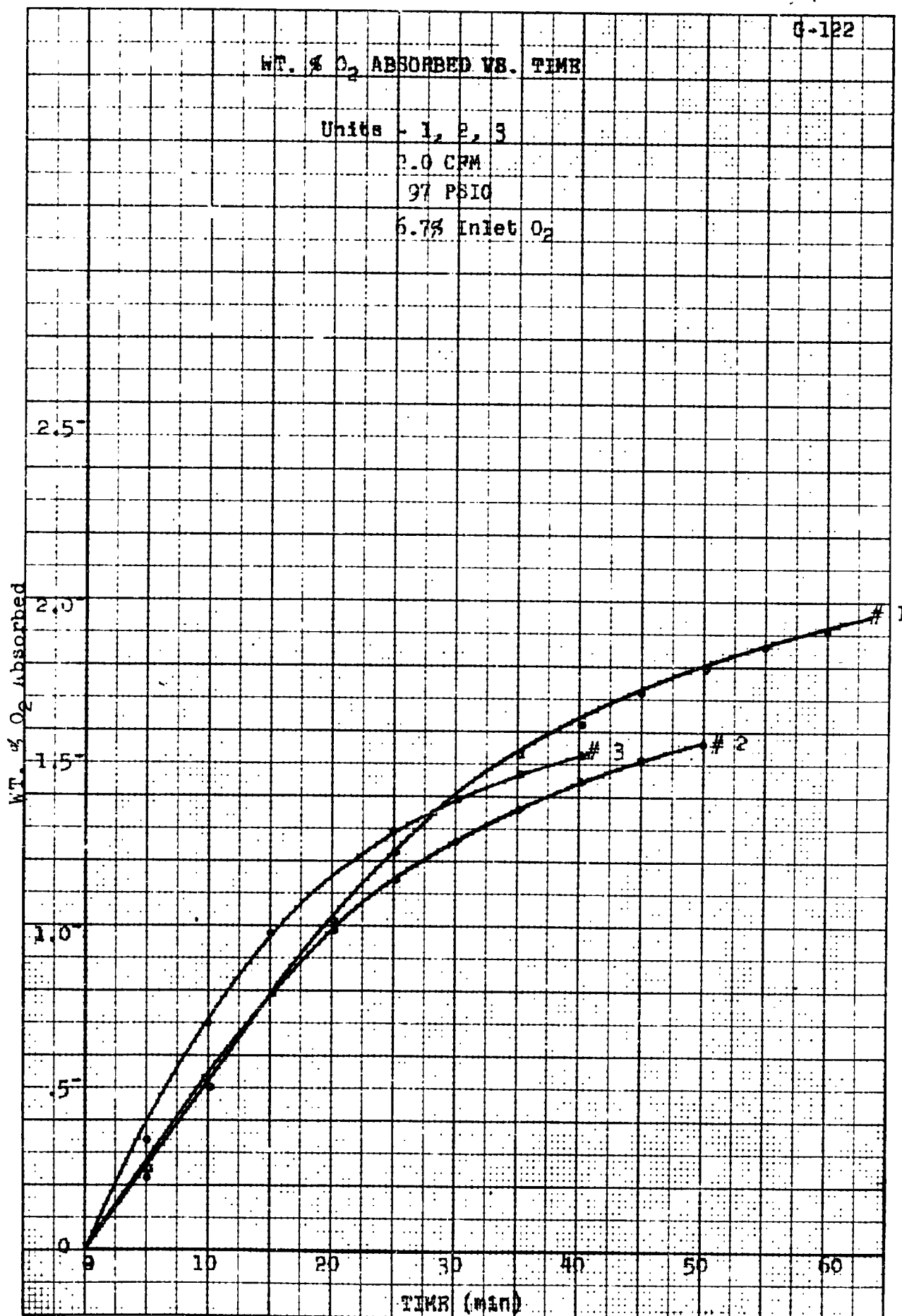


Figure 7



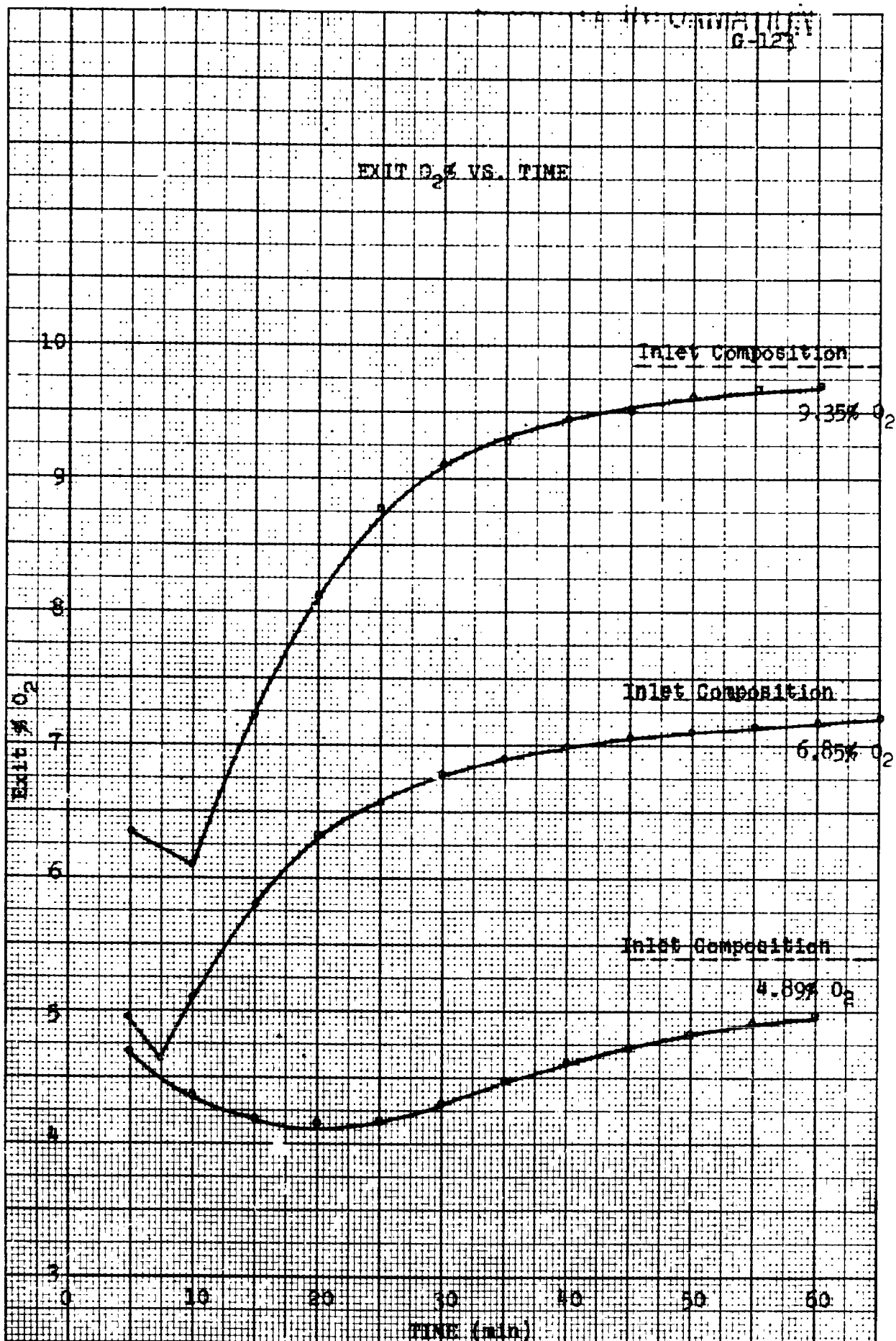


Figure 8

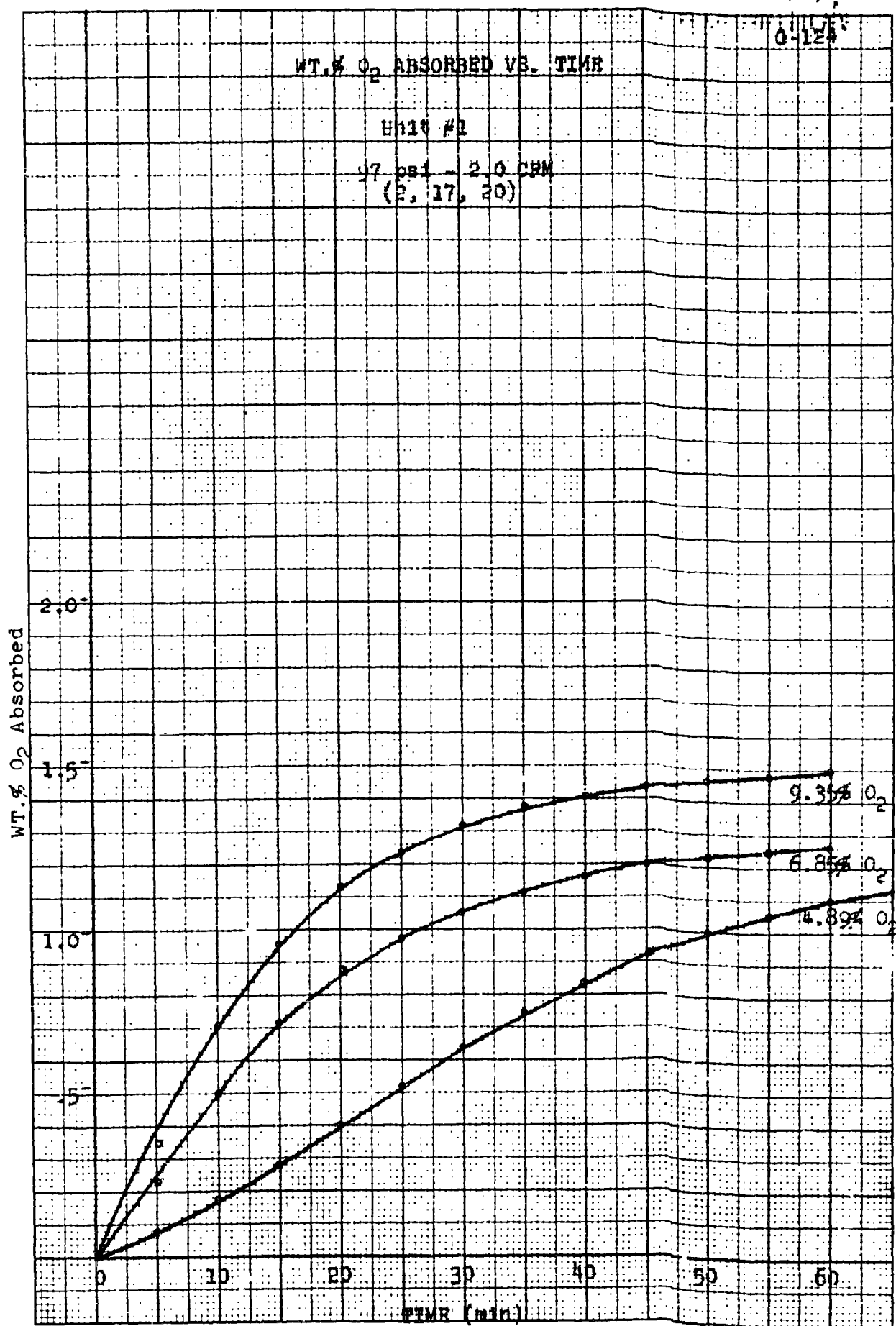


Figure 9

